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1. Doc

US 6,954,491

L7: Entry

File: 01

Dec 17, 2002

US-PAT-NO: 64
DOCUMENT-IDENT

US 6,954,491 B1

TITLE: Multil
adhesion prop

Diffusion barrier structure for improving

Full	Title	CL
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REVIEWS

REF-SEQ

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and (IDEAT or TMAT)

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L5: Entry 3 of 4

File: USPT

Nov 6, 2001

DOCUMENT-IDENTIFIER: US 6313035 B1

TITLE: Chemical vapor deposition using organometallic precursors

Brief Summary Text (10):

This invention, in one respect, relates to a method of depositing a multi-component oxide layer on a semiconductor substrate by exposing the semiconductor substrate to gaseous organometallic precursor and a reactive gas under conditions effective to cause the gaseous organometallic precursor and reactive gas to combine and deposit a multi-component oxide layer on the semiconductor substrate.

Brief Summary Text (13):

In another respect, this invention relates to a method of depositing a layer of titanium silicon oxide on a semiconductor substrate. The method comprises the steps of positioning the semiconductor substrate within a semiconductor processing chamber, and introducing gaseous reactants including titanium organometallic precursor, reactive silane-based gas and gaseous oxidant into the semiconductor processing chamber under conditions effective to cause the gaseous reactants to deposit a layer of titanium silicon oxide on the semiconductor substrate.

Brief Summary Text (15):

In another respect, this invention relates to a method of depositing a multi-component layer comprising two or more nitrides on a semiconductor substrate by exposing the semiconductor substrate to gaseous organometallic precursor and reactive gas under conditions effective to cause the gaseous organometallic precursor and reactive gas to combine and deposit a multi-component layer on the semiconductor substrate.

Detailed Description Text (4):

Multi-component films also include multi-component oxide films. By "multi-component oxide film" it is meant that a film is comprised of at least one dielectric or conductive oxide compound in combination with another material. Examples of such multi-component oxide films include, but are not limited to, films containing more than one oxide compound or films containing a mixture of oxide and nitride compounds. These films may be deposited using more than one organometallic precursor, or by using an organometallic precursor and other reactive gases, such as a reactive silane-based gas and/or a gaseous oxidant. In the practice of this disclosed method, it is typical that deposition of these films occur at low temperatures and in the absence of plasma to activate deposition.

However, those skilled in the art will recognize that benefits of the disclosed method may also be obtained at higher process temperatures and by using plasma.

Detailed Description Text (6):

Although titanium silicon oxide is deposited in one embodiment, other multi-component oxide films may be deposited using different gaseous reactants. These other films include, but are not limited to dielectric films such as tantalum silicon oxide, mixtures of titanium oxide and silicon nitride, mixtures of aluminum oxide and silicon oxide, mixtures of aluminum oxide, silicon oxide and titanium oxide and other combinations of these and other compounds. Also included are conductive films including a ruthenium oxide component, such as mixtures of titanium nitride and ruthenium oxide. During deposition, energy is supplied to a semiconductor substrate to cause a reactive deposition to take place, resulting in deposition of mixed phase metal silicon oxide onto the substrate surface. The process may be carried out in any semiconductor processing chamber or other environment known to the art that is suitable for depositing thin films on semiconductor substrates from organometallic precursors. For example, commercially available deposition equipment from suppliers such as Applied Materials, Novellus and/or Genus may be utilized. Particular models of such equipment include Applied Materials 5000D, Novellus Concept I and Genus 8700.

Detailed Description Text (8):

In one embodiment of the disclosed method, titanium organometallic precursors of the formula $Ti(NR_{sub.2})_{sub.4}$ may be used, where R is selected from the group consisting of H and a carbon containing radical, such as an alkyl. Specific examples of suitable titanium precursors include tetrakisdimethyl aminotitanium $[Ti(N(CH_{sub.3})_{sub.2})_{sub.4}]$ (TDMAT) and tetrakisdialkylamino titanium $[Ti(N(R_{sub.2}H)_{sub.5})_{sub.2})_{sub.4}]$ (TDEAT). Other suitable titanium precursors include bis(2,4-dimethyl-1,3-pentadienyl) titanium (BDPT), cyclopentadienyl cycloheptatrienyltitanium ($CpTiCht$) and biscyclopentadienyltitanium diazide ($Cp_{sub.2}Ti(N_{sub.3})_{sub.2}$). TDMAT is the typically used titanium precursor. Organometallic precursors, such as TDMAT, are typically liquid and may be vaporized for the CVD reaction. In other cases the organometallic precursor may be a solid which is sublimed to a vapor for reaction in the CVD chamber, such as bis(ethene 1,2-(N,N'-dimethyl) diamide) titanium (IV), cyclooctatetraenyltitanium, and tri(cyclooctatetraene) dititanium. In the practice of the disclosed method, a carrier gas, reactive gas or mixtures thereof may optionally be utilized to assist in vaporization and/or transportation of an organometallic precursor.

Detailed Description Text (9):

Because titanium organometallic precursors are used as a Ti source rather than titanium tetrachloride, the disclosed method offers the advantage of depositing titanium silicon oxide layers that are substantially free of chlorine related impurities when non-chlorine containing silicon reactive gases are used.

Detailed Description Text (12):

In the present embodiment, the typical gaseous oxidant is O.sub.2. However, any other gaseous oxidant containing oxygen would be suitable, for example, ozone (O.sub.3), nitrous oxide (N.sub.2 O), nitrous dioxide (NO.sub.2), or high temperature mixtures of oxygen and water vapor or oxygen and hydrogen. The carrier gas may be selected from a noble or nonreactive inert gas, such as helium, argon or nitrogen, or alternatively may be a reactant gas, such as a gaseous oxidant, hydrogen or other reactive gas. Typically the carrier gas is argon.

Detailed Description of the Invention (16):

Using the disclosed method, deposition of titanium silicon oxide is typically carried out in the absence of plasma in a cold wall CVD reactor. However, the method may also be practiced in other types of environment or semiconductor processing chambers, including, for example, in a non-plasma hot wall CVD process, a plasma cold wall or hot wall CVD process, or in a radiant energy or rapid thermal CVD process. When carried out in the absence of plasma, the method offers advantages of substantially eliminating the creation of leakage damage centers in deposited dielectric layers and of incorporating substantially no hydrogen into these deposited layers.

CLAIMS:

6. The method of claim 4, wherein the gaseous titanium organometallic precursor comprises at least one of tetrakisdimethylamino titanium (TDMAT), tetrakisdiethylamino titanium (TDEMAT), titanium ethoxide, titanium tetra-i-propoxide or a mixture thereof.

9. The method of claim 3, wherein the gaseous titanium organometallic precursor comprises at least one of tetrakisdimethylamino titanium (TDMAT), tetrakisdiethylamino titanium (TDEMAT), titanium ethoxide, titanium tetra-i-propoxide or a mixture thereof.

14. The method of claim 8, wherein the step of exposing comprises the steps of:

positioning the semiconductor substrate within a semiconductor processing chamber; and

introducing the gaseous titanium organometallic precursor, reactive silane-based gas and gaseous oxidant into said semiconductor processing chamber.

15. The method of claim 8, wherein the step of exposing comprises the steps of:

positioning the semiconductor substrate within a semiconductor processing chamber that is a non-plasma, cold wall, chemical vapor deposition (CVD) chamber;

pressurizing the chamber; and

heating the semiconductor substrate to a temperature, said pressure

WEST**End of Result Set**

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L7: Entry 1 1

File: USPT

Dec 17, 2002

DOCUMENT-IDENTIFIER: US 6495449 B1

TITLE: Multilayered diffusion barrier structure for improving adhesion propertyAbstract Text :

A method has been provided for improving the adhesion of copper to a nitrided metal diffusion barrier material, such as TiN, in an integrated circuit substrate. The method provided a multilayered diffusion barrier structure, comprising a nitrided metal diffusion barrier layer and an oxy-nitrided metal layer. The formation of an oxy-nitrided metal layer, instead of an oxide layer, permits the optimization of both contact resistance and adhesion property. The oxy-nitrided metal layer is formed either by the partial incorporation of oxygen into the nitrided metal diffusion barrier or by deposition in an oxygen ambient.

Brief Summary Text (2):

This invention relates generally to integrated circuit processes and fabrication and more particularly, to a method of improving the adhesion property of a diffusion barrier structure.

Brief Summary Text (9):

Various means have been suggested to deal with the problem of copper diffusion into integrated circuit materials. Several materials, including metals and metal alloys, have been suggested for use as barriers to prevent the copper diffusion process. The typical conductive diffusion barrier materials are TiN, TaN and WN. Addition of silicon into these materials, TiSiN, TaSiN, WSiN, could offer improvement in the diffusion barrier property. For non-conductive diffusion barrier, silicon nitride has been the best material so far. However, the adhesion of copper to these diffusion barrier materials has been, and continues to be, an IC process problem.

Brief Summary Text (11):

In a typical copper CVD process, copper is combined with a ligand, or organic compound, to make the copper volatile. That is, copper becomes an element in a compound, called precursor, that is vaporized into gas. Selected surfaces of an integrated circuit, such as that of diffusion barrier materials, are exposed to the copper gas in an elevated temperature environment. When the copper gas compound decomposes, copper is left behind on the selected surfaces. Several copper precursors are available for use with the CVD process. It is generally accepted that the configuration of the

copper precursors, at least partially, affects the ability of the copper residue to adhere itself to the selected surfaces. Although certain precursors may improve the copper adhesion process, variations in the diffusion barrier surfaces to which the copper is applied, and variations in the copper precursors themselves, often result in unsatisfactory adhesion of copper to a selected surface.

Brief Summary Text (13):

It has become a standard practice in the semiconductor industry to apply CVD copper immediately after the deposition of the diffusion barrier material to the integrated circuit to improve the adhesion and to reduce the contact resistance. Typically, the processes are performed in a single chamber or an interconnected cluster chamber. It has generally been thought that the copper layer has the best chance of adhering to the diffusion barrier material when the diffusion barrier material surface is clean and free of contaminants. Hence, the diffusion barrier surface is often kept under vacuum or in a controlled environment, and the copper is deposited on the diffusion barrier as quickly as possible. However, even when copper is immediately applied to the diffusion barrier surface, problems remain in keeping the copper properly adhered.

Brief Summary Text (14):

Charneski et al., U.S. Pat. No. 5,909,637, entitled "Copper adhesion to a diffusion barrier surface and method for same", proposed a method to use reactive gas species to clean the surface of the diffusion barrier to improve the adhesion to the subsequently deposited copper layer. This method has very limited success and often does not provide enough adhesion to be practical. Nguyen et al., U.S. Pat. No. 5,913,144, entitled "Oxidized diffusion barrier surface for the adherence of copper and method for same", further proposed a method to use reactive oxygen species to oxidize the diffusion barrier surface to improve the adhesion to the subsequently deposited copper layer. This method works well to improve the adhesion property, but by oxidizing the barrier material, it produces a non conductive layer that significantly increases the contact resistance of the integrated circuit even at a very small thickness.

Brief Summary Text (15):

It would be advantageous to understand the mechanism of the adhesion of CVD copper to a diffusion barrier material surface.

Brief Summary Text (16):

It would be advantageous to employ a method of improving the adhesion of CVD copper to a diffusion barrier material surface without oxidizing the diffusion barrier, without producing a non conductive layer and without increasing the contact resistance.

Brief Summary Text (17):

It would be advantageous to employ a method of improving the adhesion of CVD copper to a diffusion barrier material surface that can be optimized with respect to the contact resistance.

Brief Summary Text (18):

Accordingly, a method of improving the adhesion to the diffusion barrier surface is provided based on the analysis and understanding

of the properties of the diffusion barriers. A good diffusion barrier, by definition, does not allow foreign materials to diffuse through. It also has poor chemical bonding with many foreign materials. It is not thermodynamically favorable for the diffusion barriers to react with other materials because the resultant heat of formation is negative, that is, additional energies are required for these reactions. Therefore the adhesion property of good diffusion barrier materials based on chemical reaction is very poor. Deposition techniques that depend on chemical reactions to provide strong adhesion, such as chemical vapor deposition or electrochemical plating techniques, will be much more difficult to achieve good adhesion. In addition, copper material does not adhere well to many other materials, and thus adhesion of CVD copper to the diffusion barrier is even more difficult.

Brief Summary of Text (19):

From thermodynamic arguments, good diffusion barriers for copper thus are those that have a positive heat of formation with copper. The nitrided metal diffusion barriers such as TiN, TaN, WN, TiSiN, TaSiN, WSiN, composed of mainly nitrogen and other metallic components such as Ti, Ta, W, offer the best conductive diffusion barrier properties against copper diffusion. Copper nitrides have positive heat of formation so that it is thermodynamically unfavorable for copper to bond to nitrogen. These nitrides are more thermodynamically stable than copper nitrides and thus are effective against copper bonding and diffusion. Of all the mentioned nitrides, TiN and WN are similar to each other. TaN is a somewhat better barrier than either TiN or WN, and thus adhesion of CVD copper to TaN is much more difficult to achieve than to TiN or WN. The adhesion property of copper to an effective diffusion barrier however is poor.

Brief Summary of Text (20):

To improve the adhesion of the nitrided metal diffusion barrier to copper, it is operative to change the surface properties of the nitrided metal diffusion barrier layer. This surface should contain materials that bond with copper. Thermodynamically, it means that the compound in reactions of this material and copper should have a negative heat of formation, such as a copper oxide. One way to change the surface properties of the nitrided metal diffusion barrier thus is to form an oxy-nitride layer on the surface by oxy-nitriding the nitrided metal diffusion barrier layer surface, and the presence of oxygen in the oxy-nitride layer would promote the adhesion of copper to the diffusion barrier. The oxy-nitride layer comprises the metal, nitrogen, and oxygen, and serves to improve the adhesion of the multilayered diffusion barrier structure to the subsequently deposited layer. As oxygen is incorporated on the nitrided metal diffusion barrier surface, the surface becomes an oxy-nitrided metal, and no longer has the strong property. This surface thus exhibits strong property with the subsequent deposited layer. Furthermore, this thin oxy-nitrided layer is conductive and thus the contact resistance is reduced. The amount of oxygen in the oxy-nitride layer however has a strong effect on the contact resistance. The oxidizing contact will produce an oxide layer, however thin, that raises the contact resistance because of its non conductive property. Care should be taken to avoid the extreme case of

oxidizing the
introducing
over-oxidizing
small amount
contains oxygen
introduction
reduces oxidation
adhesion of
introducing
nitrided metal
diffusion, and
adhesion property
small such that
results in a

nitrided metal diffusion barrier that occurs by
excessive amount of oxygen. One way to avoid
the nitrided metal barrier surface is to introduce a
oxygen-nitride contained gas or a precursor that
and nitrogen to the barrier surface. The
the oxygen-nitride or oxygen-nitrogen combination
of the surface. Therefore a method to improve the
nitrided metal diffusion barrier without
non-conductive oxide layer is to have a multilayer: a
diffusion barrier layer to block foreign material
thin oxy-nitrided metal layer to provide the
adhesion. The oxygen content in this oxy-nitrided layer is
the nitrided metal layer is not oxidized and
conductive layer.

Brief Summary

In the oxy-nitrided
metal diffusion
nitrogen can
the ambient.
oxygen, nitride
introduce a
nitrided metal
metal layer
nitrided metal
oxygen-containing
improvement
barrier, and
diffusion barrier
diffusion barrier
nitrogen from
ambient source
diffusion barrier
together with
diffusion barrier
good adhesion

it (21):

During the nitriding process, the metal comes from the nitrided
barrier layer, oxygen comes from the ambient, and
nitrogen comes from the nitrided metal diffusion barrier layer and
there are different ways of incorporating the metal,
to form the oxy-nitride layer. One way is to
introduce a small amount of oxygen to a thin surface of the
diffusion barrier. To provide a thin oxy-nitrided
layer, as TiCN, TiSiCN, TaCN, TaSiCN, WCN, WSiCN, the
diffusion barrier surface is oxy-nitrided in an
ambient. The oxy-nitrided metal adhesion property
is most effective with TiCN, a less effective diffusion
barrier, a less effective with TaCN, a more effective
diffusion barrier. This method uses the nitrogen from the nitrided
barrier layer. Another way is to introduce oxygen and
nitrogen from the ambient. Additional nitrogen thus comes from the
ambient. Another way is to deposit a thin oxy-nitride metal
layer or using an oxygen/nitrogen precursor
precursors needed to deposit the nitrided metal
layer. Not all oxy-nitrided materials however exhibit
good adhesion property.

Brief Summary

Cleaning the
al., in U.S.
it does not
barrier surface
by Nguyen et al.
improving the
adhesion is
layer with the
oxygen plasma
resistance to
limiting the
on the tunneling

it (22):

For the diffusion barrier, a method proposed by Charneski et al.
No. 5,129,637 has a very limited success because
it does not take into account the fundamental properties of the diffusion
barrier. Oxidizing the diffusion barrier, a method proposed
in U.S. Pat. No. 5,13,144, is a proper method of
improving the adhesion property. However, the improvement in
adhesion is not by the introduction of a non-conductive oxide
layer of reactive oxygen species from a predominately
oxygen plasma. Nguyen et al.'s method solved the high contact
resistance related to the non-conductive oxide layer by
making the thickness of this layer to less than 3 nm and relying
on the tunneling phenomenon to provide the conduction path.

Brief Summary

An improved
nitrided metal
layer. The
nitrogen, and
species being

it (23):

A method to improve adhesion is to form a multilayer: a
diffusion barrier layer and a thin oxy-nitride metal
oxy-nitride metal layer comprises the metal,
oxygen, and the same oxy-nitride metal, the oxygen
content is less than the nitrogen species, that works best since

it is much more
does not differ

conductive than an oxide, and the adhesion property
significantly.

Brief Summary

Accordingly,
the nitrided
TaSiN, WN, W
structure is
is deposited
subsequently
Depositing a
underlayer
this diffusion
underlayer a
metal nitride
diffusion bar
comprises the
less than the
improve the
structure to

(24):

Method to improve the adhesion property of copper to
diffusion barriers such as TiN, TiSiN, TaN,
by forming a multilayered diffusion barrier
provided. The provided multilayered diffusion barrier
an underlayer, and provides improved adhesion to a
situated layer. The method comprises the steps of: a)
provided metal diffusion barrier layer on the
diffusion barrier deposition equipment, whereby
barrier layer serves as a barrier between the
a subsequently deposited layer; b) Forming a thin
oxy-nitride layer by oxy-nitriding the
material surface, this oxy-nitride layer
al, nitrogen, and oxygen, the oxygen species being
nitrogen species, whereby this layer serves to
adhesion of the multilayered diffusion barrier
subsequently deposited layer.

Brief Summary

The two layers
oxy-nitrided
includes the
locations: the
in two separate
metal diffusion
the two chambers
substrate will
two chambers
oxy-nitriding
oxy-nitride
In some aspects
provided. The
1200.degree
temperature
to several
optimization
of adhesion

(25):

Nitrided metal diffusion barrier layer and the
layer are formed in sequence. The method
formation of these two layers in two separate
process chambers in the same process equipment, or
process equipment. The formation of the nitrided
barrier will occur in the first process chamber (of
equipment). Then in the first process equipment. The
substrate will be moved to the second process chamber (of the
equipment), to the second process equipment for the
process. The oxy-nitriding process to form the
layer will require an oxygen-contained ambient.
of the invention, an elevated temperature is also
related temperature ranges from 200.degree. C. to
with 300-600.degree. C. being a typical
The oxy-nitriding time ranges from a few seconds
to several minutes, depending on many factors such as the
process flow, the optimization of the desired level
of adhesion optimization of contact resistance, etc.

Brief Summary

The method
the surface
nm. The 5 nm
adhesion, a
multilayered
as the ones
overall diff
thin metal
adhesion is

(27):

provides the thickness of the oxy-nitride layer on
provided diffusion barrier to be less than 5
nm. The 5 nm thin metal oxy-nitride layer offers adequate
adhesion, a multilayered diffusion barrier structure. Some applications, such
as the ones used in semiconductor processing, require that the
overall diffusion barrier thickness to be less than 50 nm, so a
thin metal diffusion barrier is desirable, provided that adequate
adhesion is provided.

Brief Summary

The method
metal diffusion
nitrided metal
The sputter

(28):

requires that one uses to deposit the nitrided
layer. The evaporation technique can deliver the
nitrided metal layer by depositing the source material.
The sputter technique can deliver the nitrided metal diffusion